The Collision-Induced Dissociation Dynamics of Diatomic Ions at High Levels of Vibrational Excitation

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INTRODUCTION

The modeling of an increasing number of technical and natural environments at extreme conditions involves gas-phase dynamics far from equilibrium. Consequently, a correct representation of the system on a molecular scale requires knowledge of the state-to-state dynamics and how it couples to macroscopic dynamics. While a considerable body of work exists on state-to-state molecular dynamics, experiments have generally been limited to low levels of excitation due to limitations in existing reactant state-preparation techniques.

The vibrational energy dependence of collision-induced dissociation (CID) of diatomic neutrals and ions is of fundamental importance in the understanding of rarefied shocks such as those generated upon atmospheric reentry of spacecraft. In the present project, we exploit the ALS brightness and the world-class photoionization apparatus of Endstation 9.0.2.2 to prepare ions in well-defined vibronic states.[1] To date, studies of state-selected ions have relied on direct photoionization or multiphotoionization where the number of accessible states is limited by Franck-Condon factors.[2] We have devised an experiment where we prepare diatomic ions by resonantly exciting the precursor neutral molecules using monochromatic synchrotron radiation to long-lived Rydberg states that lie within a few wavenumbers near the ionization limit of a particular vibronic state. The experiment will make use of a micro-machined chopper inserted in the beamline to generate an extended, controllable dark gap. Electrons and associated ions produced in direct ionization to lower vibronic states will be swept away by a weak electric field. During the dark gap, following a delay of ~100 ns after its onset, a strong pulse will be applied to field ionize the remaining excited molecules (pulsed field ionization). A beam of diatomic ions in a pure vibrational state will thus be generated by the judicious choice of the respective field strengths and the associated timing. The photon energy dependence of pulsed-field ionized (PFI) electron intensities have demonstrated that diatomic ions are produced over a broad range of internal energies approaching the dissociation limit. For example, ALS experiments at Endstation 9.0.2.2 were able to observe the last vibrational level of H_2^+.[3] Thus, state-resolved dynamics should be possible over an unprecedented range of internal energies.

In the following, we describe the ion-molecule reaction experiment currently being constructed at Endstation 9.0.2.2. The initial experiments to be conducted on the newly built apparatus will then be discussed.

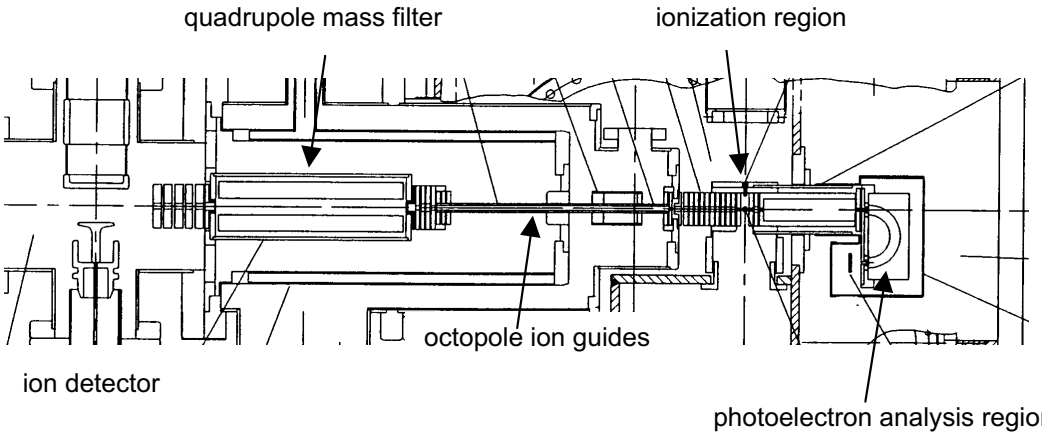

Figure 1. Schematic of ion-molecule reaction experiment under construction at Endstation 9.0.2.2.

EXPERIMENT

The new ion-molecule reaction experiment will use the proven guided-ion beam (GIB) technique[4,5] to study the translational energy dependence of CID cross sections of state-selected diatomic ions. State-selected ions will be generated using monochromatic synchrotron radiation and PFI as described earlier (see Fig. 1). Ions extracted from the PFI region of Endstation 9.0.2.2 will be injected into an rf-only octopole ion guide system consisting of 2 ion guides (2 mm rod diamater, 6 mm inner diameter) in tandem. The first octopole (8.64 cm long) guides the ions through a collision cell containing the target gas. Primary and secondary ions then pass through a second octopole (19.63 cm long) before they are extracted for mass discrimination using a quadropole mass filter, and detected with a Daly detector. Arrival time spectra will also be recorded in order to deduce recoil velocity distributions and the associated scattering dynamics.

PLANNED EXPERIMENTS

Given the importance of O_2^+ ions in various extreme environments, we will first study the vibrational energy dependence of CID of this ion with various target gases. In particular, we are interested in how the cross section threshold functions scale with vibrational energy, and what the role of low-lying excited electronic states is. This past year, we have conducted preview experiments using the Hyperthermal Ion Beam Facility at the Air Force Research Laboratory.[6] A mixture of low vibrational states of O_2^+ was generated by ionizing O_2 with near-threshold electrons. By investigating Ar and Ne targets, the effect of the charge-transfer surface can be explored: in case of O_2^+ + Ar collisions, the charge-transfer (CT) surface lies below the CID threshold, while for O_2^+ + Ne, it is substantially above it.

Figure 2 displays the observed cross sections. Whereas no CT channel is observed in Ne collisions at the investigated energies, CT and CID appear intimately coupled in the Ar system. Interestingly, both CT and CID have onsets that are higher than their thermochemical thresholds. Note that the weak cross section in the Ne case results in an observed threshold that is below the thermochemical limit of 6.61 eV (the above experiments also include an average internal energy of ~0.5 eV). This can be explained by contributions from multiple collision effects, given the

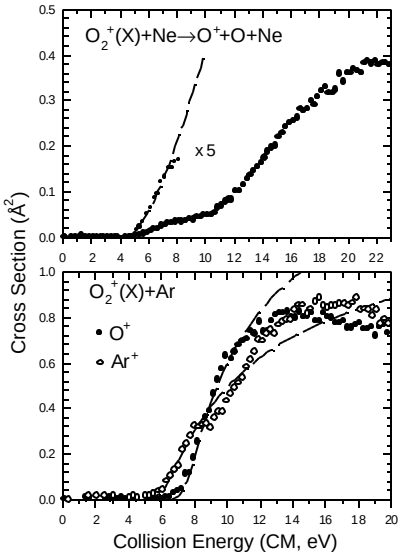

Figure 2. Energy dependence of cross sections for the reaction channels observed in O_2^+ + Ne(Ar) collisions. The dashed lines are fits to modified line-of-centers threshold functions.

very small cross sections near threshold. A second threshold around 10 eV may be attributed to the participation of a number of excited electronic surfaces, including the CT surface.

The above experiments clearly demonstrate that nonadiabatic processes become very important in high threshold cases requiring substantial translational energy. The experiments at Endstation 9.0.2.2 will allow us to systematically change the threshold energy through vibrational population of the reactant ion, which should eventually lower the nonadiabaticity of the dynamics near threshold, thereby decoupling CT and CID at low energies.

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